New Developments in Flame Retardancy of Glass - Reinforced Epoxy Composites

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ABSTRACT

This work involves development of novel glass fibre-reinforced composite materials containing a commercially available epoxy resin, a phosphate - based intumescent and inherently flame retardant cellulosic (Visil, Sateri) and phenol-formaldehyde (Kynol) fibres. The intumescent and flame retardant fibre components are added both as additives in pulverized form and fibre interdispersed with intumescent as a fabric scrim for partial replacement of glass fibre. Thermal stability, char formation and flammability properties of these novel structures are studied by thermal analysis, LOI and cone calorimetry. The results are discussed in terms of effect of individual additive component on thermal degradation / burning behaviour of neat resin.

Key words : epoxy ; composites ; flame retardancy ; intumescents ; heat release

1. INTRODUCTION

Epoxy resins constitute the organic matrix for high performance composite materials used in the fabrication of light structural panels for an aircraft and other transport. The major advantages of these composite structures over traditional metallic materials like steel and aluminium are their favourable mechanical, physical - chemical properties and high strength- to-weight ratio. In order to increase the market penetration and because of current stringent aviation and other legislation to increase safety, improvements in flame retardancy have been given significant priority. Since these resins cross-link on curing, their char-forming tendency and hence thermal stabilities can be increased by adding suitable additives. The ability to tailor the properties of composites makes it feasible to do this and examples are described in this paper

Intumescents are widely used as surface coatings for effective flame retardant treatments.[1,2] However, they can be used as additives for thermoplastic and thermoset polymers [3-5] as char promoters. In our previous work [6,7] we have observed that phosphate - based intumescents interact with flame-retardant (FR) cellulosic fibres during the application of heat and form a complex 'char-bonded' structure. The char formed is greater in mass, resistant to oxidation, has better thermal barrier properties and higher mechanical strength compared to individual components. We then extended this research to enhance char formation of thermoset (epoxy, phenolic and polyester) resins used in glass - reinforced rigid composites.[8] When studied by thermal analytical techniques, it has been observed that the introduction of an intumescent/flame retardant cellulosic fibre (Visil, Sateri) to these resins results in physical and chemical interactions of three components leading to enhanced char formation.[9,10] The results indicated that laminates produced from these components should have superior flame-retardant properties. The intumescent /FR fibre combinations may be introduced either as a pulverized additive to the

resin or as an additional textile fabric layer to the composite structure.[8] In our previous work we prepared such structures with polyester resins, studied their flammability and mechanical properties and effect of different variables on these properties.[11] In general it was observed that inclusion of intumescent and flame retardant cellulosic fibre to polyester resin slows down their burning process measured in terms of heat release rates.

In the present work similar structured epoxy composite laminates are prepared and studied for their flammability properties. Some of the structures contain another flame-retardant and high performance fibre, Kynol (Kynol, Japan) and their properties are compared with samples containing Visil fibre. Compatibilty of the Kynol fibre and resin with and without intumescent is studied by thermal analysis.

2. EXPERIMENTAL

2.1. Samples (i) – (vi)

Materials :

Resin : B3B – a multifunctional epoxy resin (Hexcel Composites Ltd, UK)

Glass : E-glass in the form of woven roving (300 gm^{-2}), supplied by Glassplies, Southport, UK

Flame-retardant (FR) fibre : Visil (Sateri Fibres, Finland) – cellulosic fibre containing polysilicic acid, in pulverised form (from original fibre length 40 mm, 3.5 dtex and diameter 17 μm)

Kynol, KF – 10 BT in powder form (average fibre length 0.33 mm, diameter 33 μm)

Intumescent : Antiblaze NH (Rhodia Specialities Ltd) – contains melamine phosphate

Samples :

(i)	Ep	-	8 layers of woven glass // resin
(ii)	Ep + NH	-	8 layers of woven glass // resin + NH
(iii)	Ep + Vis	-	8 layers of woven glass // resin + Visil
(iv)	Ep + Vis + NH	-	8 layers of woven glass // resin + Visil + NH
(v)	Ep + Ky	-	8 layers of woven glass // resin + Kynol
(vi)	Ep + Ky + NH	-	8 layers of woven glass // resin + Kynol + NH

Composite laminate preparation

Samples were prepared by impregnating glass fabric with resin and/or additive(s). Individual fabric layers impregnated with resin were dried in an oven at 40^0C for 10 min. All the layers were stacked, laid up in vacuum bags and cured at 135 ^{0}C for 1 hour in an autoclave.

The performance of composites is dependent on the properties of the materials comprising the composite and the process by which they are combined. It also very much depends on the type and amount of resin used. Hence for comparison reasons, the conditions and amounts of different components are kept constant. To keep the resin weight same in all the samples, sample (iv) was impregnated first. It contains 50% (w/w) glass and 50% (w/w)resin + additives. For other samples the resin content was kept same

and all additives are additional. Intumescent in sample (i) is 10% (w/w) with respect to resin. FR fibre in samples (iii) and (v) is also 10 % (w/w) with respect to resin. In samples (iv) and (vi) FR fibre+NH is 20% (w/w) with respect to resin. However, the amounts of the components present in final laminates as given in Table 1 are different as these are the percentages within the respective final products.

2.2. Samples (vii) – (ix)

Materials :

Resin : A film of multifunctional epoxy resin (120 gm^{-2} area density) was prepared commercially by Hexcel Composites Ltd.

Glass : E-glass in the form of woven roving (300 gm^{-2}).

Flame-retardant (FR) fibre : Visil–NH (240 gm^{-2}). Prepared by padding on non woven web of Visil (120 gm^{-2}) with intumescent (100 % w.r.t. fibre wt) and Vinamul 3303 resin (15% w.r.t. intumscent).

Kynol (80 gm^{-2}) in the form of non-woven mat.

Intumescent : Antiblaze NH

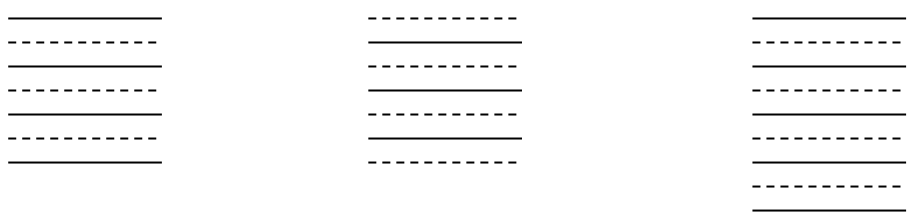
Samples :

(vii) 4Gl-3Vis-NH - 4 layers of glass and 3 layers of Visil-NH sandwiched in between //resin

(viii) 4Vis-NH-3Gl - 4 layers of Visil-NH and 3 layers of glass sandwiched in between //resin

(ix) 5Gl-4Ky - 5 layers of glass and 4 layers of Kynol sandwiched in between //resin

The structures of these samples can be represented schematically as below :



(solid line is glass and broken line Visil-NH / Kynol fabric)

Sample (vii) Sample (viii) Sample (ix)

Scheme.1. Schematic representation of structures of samples (vii)–(ix)

Composite laminate preparation

Samples were prepared by using resin film (prepared and supplied by Hexcel). Each layer of glass and Visil was sandwiched between two resin films, ironed on it and peeled the release paper off. All subsequent layers were stacked and then processed similar to as samples (i) to (vi).

2.3. Testing Equipment

Thermal analysis : For simultaneous DTA/TGA analysis a TA Instruments SDT 2960 was used under flowing air (100 ml/min) and at a heating rate of 10 K min^{-1}. About 10.0 mg of sample was used in each case. The pulverised fibres were used in this study.

The following combinations were studied by simultaneous DTA-TGA to observe the compatibility of different components :

- Resin, intumescent and fibre individually
- Resin / intumescent - 1 : 1 mass ratio
- FR fibre/intumescent - 1 : 1 mass ratio
- Resin // FR fibre / intumescent - 1 : 0.5 : 0.5 mass ratio

Limiting oxygen index (LOI) : A Stanton-Redcroft LOI FTA analyser was used to determine LOI values according to the standard procedure.[12]

Cone calorimetry : A cone calorimeter (Fire Testing Technology Ltd., UK) was used at an incident heat flux of 50 kWm^{-2} in an air atmosphere under free convective air flow conditions according to ISO 5660.[13] Composite samples (100 x 100 mm size) were wrapped in aluminium foil and placed in a specimen holder over a ceramic blanket at least 13mm thick. Spacing of 25 mm was maintained between the bottom of the cone and top of the specimen. All the tests were performed with the retainer frame in place as recommended in ISO 5660-1, which helped in reducing edge effects and composite delamination. Since these samples do not intumesce in a conventional way and the intumescent chemicals react with the FR fibre (Visil) and resin to form a char-bonded structure,[9,10] then no extra surface grid to stabilise the samples was required.

3. RESULTS AND DISCUSSION

3.1. Thermal analysis of component mixtures

Thermal analytical results and thermal degradation mechanisms of epoxy resin, Visil, intumescent Antiblaze NH (melamine phosphate) used in the present study and their different combinations are discussed in detail in our previous communications.[9,10] As for the present work, in some samples ((v), (vi) and (ix)) Visil fibre is replaced by another high performance Kynol fibre, thermal analytical studies of all the combinations with Kynol were carried out and here results are compared with the combinations containing Visil fibre

In Fig.1(a) char yield differences between expected and calculated average values from TGA curves of individual components of fibre-intumescent and resin-fibre mixtures are plotted as functions of temperature. The details of interaction of both Visil and Kynol with melamine phosphate are discussed elsewhere.[9,10,14,16] As can be seen from Fig.1(a), the Kynol and melamine phosphate mixture shows evidence of greater interaction than Visil – melamine phosphate in the 470 – 680 ^{0}C temperature range. However, above 700 ^{0}C, the Visil-intumescent system is more stable than Kynol-intumescent. The TGA response showed that the former has 17 % residual char left whereas, Kynol-intumescent char is totally oxidized and corroborates this observation. This indicates the Visil fibre and melamine phosphate are interacting to produce a 'char-bonded' structure, which is comparable (and better at high temperatures) in performance to the one involving high performance (Kynol) fibre.

When compatibility of each fibre with epoxy resin is studied, although the resin-Visil mixture shows more-than-expected char formation in the temperature range 300-500 ^{0}C (Fig.1(a)), the original DTA curves indicated no significant interaction.[9,10] This greater char formation may be a physical effect in that both Visil and resin exert a initial "filler effect" on each other, producing slightly more char than expected, which then oxidises. Kynol on the other hand promotes char formation in the temperature range 370 – 600 ^{0}C, which indicates some interaction between the cross-linking resin and the phenol-formaldehyde structure in the fibres.

The DTA and TGA results of resin/intumescent and resin/Visil/intumescent combinations showed that the behaviour of mixtures are quite different from those of individual components and their calculated averages thus indicating some kind of interaction.[9,10] The char yield differences between expected and calculated values from TGA curves in Fig.1(b) show that melamine phosphate increases char forming ability of epoxy resin upto about 730 ^{0}C. But when either fibre is present, the system becomes stable upto 900 ^{0}C and about 5% more-than-expected char residue is left behind. Detailed modes of possible interaction have been discussed elsewhere[9,10] and this chemical interaction between these components indicates that composite laminates produced from these components should have superior flame retardant properties.

3.2. Flammability of Composites

3.2.1. Limiting oxygen Index (LOI)

LOI is considered to be a measure of flammability of a sample in terms of threshold oxygen concentration for sustained burning. LOI results for composite samples are given in Table1. The value for control sample (i) is 27.5 %. The change in LOI (Δ LOI) for other samples with respect to LOI of control sample (i) are shown in Fig.2. Presence of intumescent (sample (ii)) increases LOI to 35.2, while Visil (sample (iii)) addition does not have much effect. The presence of both Visil and intumescent however, increases the value to 36.2%. In samples (i)-(iv) the same amount of glass fabric is present, hence ΔLOI for these reflects the effect of additives only. However, when Visil-NH is in fabric form (samples (vii) and (viii)), there is a greater increase in LOI values (38.4 and 34.2, respectively) probably because of more amount of Visil-int compared to sample (iv) (see Table 1) and the complex layered structures present.

Kynol both in fibre (sample (v)) and fabric (sample (ix)) form has little effect on LOI. Even when present with intumescent (sample (vi), LOI = 30.2), it is not as effective as the resin, Visil and intumescent combination (sample (iv), LOI = 36.2).

3.2.2. Cone calorimetry

Cone calorimetry enabled various parameters to be determined (see Table 2). Selected results are also shown in Figs.3-5. The results presented here are averages of three runs for each sample.

Time to ignition (TTI) : Time to ignition may be defined as the ease of ignition. For control epoxy sample TTI is 42 s. The addition of intumescent, Visil fibre and mixture of both have little effect on TTI as can be seen from Table 2. The flameout times as given in Table 2 indicate that these samples are burning for similar times. However, Kynol with and without intumescent slightly increases TTI and burn time. The TTI values for layered composite structures are quite similar, whether it is Visil-NH fabric or Kynol fabric, but the burning times are different depending upon their resin contents.

Heat release rate (HRR) : Heat release rate is the heat generated per unit time by the burning sample divided by the surface area of the sample. Hence, it is a measure of the heat release rate to the surroundings per unit surface area of the burning material. The important parameters for assessing the fire performance of a material are the maximum or peak heat release (PHRR), average heat release (AvHRR) and total heat release rates (THR). HRR curves as a function of time for samples (i)-(ix) are given in Fig.3(a-c). As can be seen from Fig.3(a) and Table 2, the presence of intumescent reduces the PHRR from 385 to 278 kW/m^2 indicating reduction in

volatile fuel formation. When both intumescent and Visil are present, the peak is further reduced to 262 kW/m^2. Presence of Visil alone (sample (iii)) also reduces PHRR value and as can be seen from HRR curve in Fig.3(a), there are two peaks, representing reduction of resin volatilisation and that derived from condensed phase activity of Visil. When both Visil and intumescent are present (sample (iv)), this effect becomes more pronounced (see Fig.3(a)). Kynol without and with intumescent has not such effect with the values being 367 and 354 kW/m^2, respectively. But as can be seen from Fig.3(b), and respective TTI and TTP (time to peak) values in Table 2, the HRR curves are shifted towards longer times, indicating that they ignite slowly and burn for longer times. This indicates that the potentially cross-linking phenol-formaldehyde Kynol may interfere with the cross-linking epoxy resin and delay its degradation and volatilisation without influencing its ultimate heat release.

When Visil-NH or Kynol fabric is used, the PHRR values are higher than control samples (see Table 2), but there is no direct comparison since resin contents for these samples are different.

THR and AvHRR values also show similar trends, with the lowest value being for sample (iv) containing Visil and intumescent, which are even lower that for sample (vi) containing Kynol and intumescent.

Effective heat of combustion (H_c) : The effective heat of combustion over a given time frame (5 min in Table 2) is the quantity of heat produced by combustion of a unit quantity of a material. It is measured in the cone calorimeter throughout the burn period from the HRR and mass loss and may thus be used to measure possible flame retarding effects of components present. Visil powder reduces the heat of combustion (19.8 MJ/kg for the control sample) in sample (iv) (16.6 MJ/kg), whereas Kynol has little effect (19.0 MJ/kg for sample (vi)) even when

present in fabric form (19.8 MJ/kg). When both Visil and intumescent are present, the value is 17.3 MJ/kg and for Kynol /intumescent mixture it is even lower (16.8 MJ/kg). This reflects the combined effect of intumescent and FR fibre components on volatile fuel formation and hence burning of the samples.

Mass loss : Since the char retained after burning a polymer is also a measure of its flammability, the mass loss curves give insight into the fire performance of the samples. Typical mass loss curves for selected samples and the effect of additives on their residual char retained after 5 minutes are given in Fig.4(a) and (b), respectively. The presence of intumescent alone and with Visil fibre increases the residual mass at any time. This supports thermal analytical results that these components promote char formation of the resin. Kynol fibre when present or with intumescent does not increase residual char of the resin. Again for samples (viii)–(ix) there is no direct comparison as resin contents are different.

Smoke : The results of smoke generation can be expressed in different forms. Here smoke formed is expressed as a function of time for some typical curves are shown in Fig.5 and total smoke formed in 5 minutes is given in Table 2. Both intumescent (sample (ii)) and Visil (sample (iii)) when present alone, reduce amounts of smoke compared to the control sample (sample (i)). When both Visil and intumescent are present there is considerable reduction in smoke (sample (iv)). However, when the Visil-intumescent combination is present in fabric form, the values are higher, but the resin and glass contents in these samples are also different than other samples. Kynol with and without intumescent is not as effective as Visil in reducing smoke but it is less than the control sample.

Carbon monoxide and carbon dioxide : Average CO and CO_2 productions in 5 minutes are given in Table 2. Visil and Kynol fibres on their own do not seem to affect CO and CO_2 values. The intumescent additive with and without fibre, reduces these values. For samples (vii)–(ix), the values are still less than or close to those for control sample.

3.3. Derived cone parameters

The fire growth rate index, FIGRA : The fire growth rate, described by Sundstrom,[17] is helpful in ranking the materials in terms of potential fire safety since it combines peak fire size (PHRR) and time to achieve this (time to peak, TTP). Thus

$$\text{FIGRA index} = \text{PHRR} / \text{TTP (kW/s)}$$ [17]

The FIGRA index values calculated for all the samples are given in Table 3. As the results show the presence of Visil fibre only (sample (iii)) reduces this index value. Intumescent presence without (sample (ii)) and with Visil (sample (iv)) reduces the value compared to control sample, but this system is not as effective as Kynol without (sample (v)) and with intumescent (vi).

Unitised HRR values : From Table 1 it can be seen that all these samples have different mass fractions of resin. Thus from the cone results given in Table 2 , for sample (i), following equation for PHRR can be written assuming that the 0.55 mass fraction of glass has zero fuel level :

$$0.45\ Ep = 385\ kW/m^2 \qquad \text{- - - - -} \quad (1)$$

to yield $Ep = 855.6\ kW/m^2$ per unit mass fraction.

In a similar manner, the following equations (each having units, kW/m^2) for samples (ii)-(iv) hold :

$$0.42\ Ep + 0.05\ Int = 278 \quad \text{- - - - -} \quad (2)$$

$$0.42\ Ep + 0.05\ Vis = 329 \quad \text{- - - - -} \quad (3)$$

$$0.40\ Ep + 0.05\ Vis + 0.05\ Int = 278 \quad \text{- - - - -} \quad (4)$$

From equations (2) - (4), the effect on PHRR values for unit mass fractions of Int, Vis and (Vis+Int) can be calculated by substituting for Ep. Similar equations can be used for samples containing Kynol (samples (v,vi)). The PHRR values calculated per unit of each additive with respect to unit resin are shown in Fig.6(a). Sample (ii)-(iv) values are negative indicating respective additive heat release rate-reducing properties. For Visil-intumesent combinations, respective calculated values (by averaging weighted component values) for each component are also given.

Fig.6(a) shows that unit mass fractions of intumescent (Int) and Visil alone reduce PHRR by 1620 and 600 kW/m^2, respectively. The combined effect of (Vis+Int) (-800 kW/m^2) is less than additive when compared with the calculated value of -1110 kW/m^2. However, Dabrowski et al [18] have shown that glass may react with phosphoric acid released from phosphate intumescents and so the simple equations (1)-(4) may only be approximate since they assume that glass is inert. Kynol and intumescent on the other hand increase the PHRR by 120 kW/m^2, whereas a decrease of 730 kW/m^2 is expected.

These unitised values are then used to calculate PHRR values for samples (iv), (vi), (vii)-(ix) and are given in Table 3. For sample (iv) the observed value is less than expected and for sample (vi) this difference is greater. Samples (vii) and (viii) show even larger differences which may be due to a layering effect of the Visil-Int fabrics present. In samples (i)-(vi) Vis and Int are added as additives and the glass fibre mass fractions are the same (8 layers, see

Section 2.1), while in samples (vii)-(ix) glass contents are different (see Section 2.2), and so may exert varying filler effects, hence giving greater inconsistency in these latter results. Moreover, because Visil (or Kynol) and intumescent in samples (iv)-(vi) are in pulverised additive forms, their high surface contact with resin will more likely to affect decomposition of resin and assist in cross-linking reactions, whereas, in samples (viii)-(ix) there will be be a reduced surface effect

Other unitised parameters : Other parameters, THR, H_c, residual mass after 5 minutes and smoke were calculated using equations similar to (1)-(4) by inserting respective values. For mass calculations, mass of the glass was substracted from the total mass residue and the results are given in Fig.6 and Table 3.

THR values show effects similar to PHRR where for example, the observed reduction in THR for Vis+Int (sample(iv)) is less-than-expected from calculated (see Fig.6(b)), and increase for Ky+Int is also less-than-expected. For Visil - containing samples (iv), (vi) and (vii), THR is more than expected, whereas for Kynol containing samples (v) and (ix), it is less than expected.

Residual mass values after 5 minutes for samples containing FR fibre and intumescent are again slightly less-than-expected, as can be seen from Fig.6(c), which is contrary to results of thermal analytical studies as shown in Fig.1. This suggests that in an actual fire situation, although these additives help in char formation (see Fig.4(b)), they do not work so efficiently under the slow heating conditions of TGA. For samples containing FR fibre and intumescent in fabric form, the lower-than-expected residual mass (see Table 3) suggests that they do not mix and interact with resin fast enough to form a ‘char-bonded’ structure.

Smoke results show trends similar to heat release parameters as can be seen from Fig.6(d) and Table 3 in that actual smoke reduction is less than calculated, although samples containing Visil show clear comparative results than Kynol analogues.

4. CONCLUSIONS

Thermal analytical results indicate that there is resin-Kynol-intumescent interaction similar to the resin-Visil-intumescent interaction observed previously.[9,10] Moreover, resin-Visil-intumescent systems are comparable and even better at enhancing residues at higher temperatures than the resin-Kynol-intumescent combination, where a high performance fibre is used. Cone calorimetric results also indicate similar behaviour in that when intumescent and FR fibre are used as additives, they reduce PHRR, THR, AvHRR and smoke values. This effect is different than the one observed for similar polyester composites[11] where, although PHRR and AvHRR were reduced, THR increased and HRR vs time curves became broader with higher flameout times. Thus, where in polyester laminates the presence of intumescent and FR fibre slowed down but prolonged burning, in the epoxy samples reported here, overall burning tendencies are reduced. However, quantitative analysis of the separate and combined effect of the additives / components suggests that any interactions are less than additive, which is contrary to the thermal analytical results. A number of differences exist between the two sets of experiments with (i) the slow heating regime in thermal analysis, (ii) the effect of layered fabrics in composites, and (iii) the assumed inertness of glass being of possible significance. Clearly, the observed-less-than additive fire performance in composites is of greatest concern and requires further investigation. Mechanical properties of these laminates and residual mechanical properties after heat / fire exposures are presented in a separate publication.

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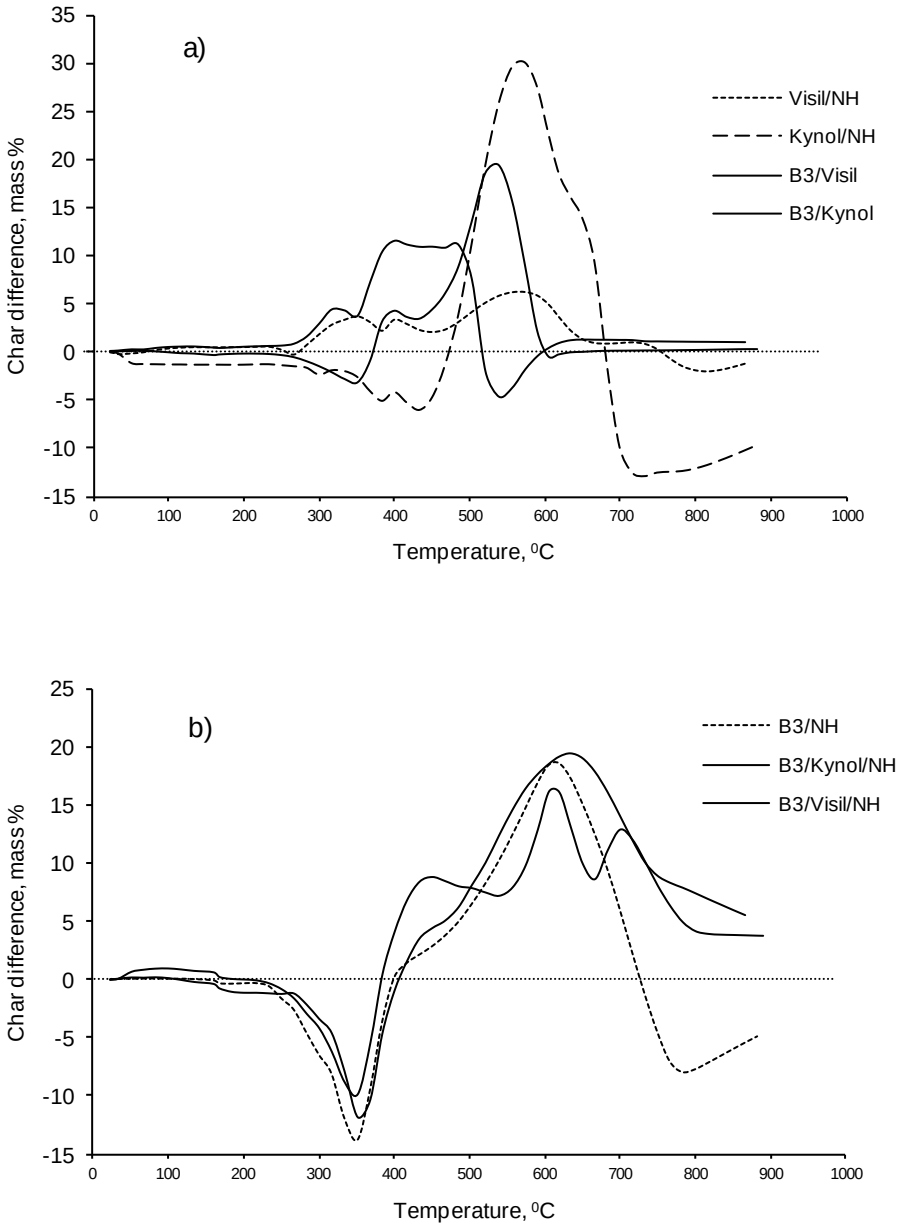


Figure 1. Percentage residual mass difference (actual-averaged) as a function of temperature for a) Visil/NH (·····), Kynol/NH (– – –), B3/Visil (——), B3/Kynol (——) ; b) B3/NH (·····), B3/Visil/NH (——) and B3/Kynol/NH (——).

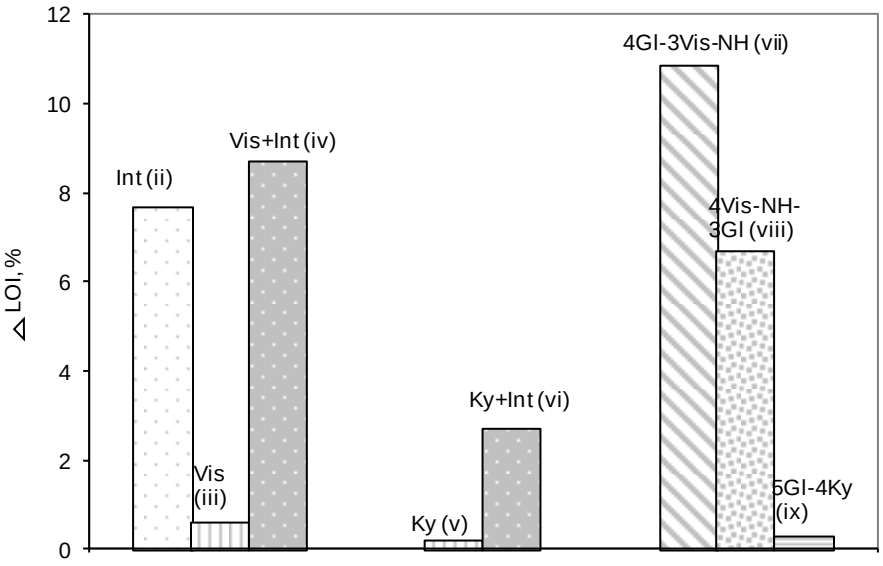


Figure 2. Change in LOI (ΔLOI, %) of samples (ii)-(ix) compared to control sample (i).

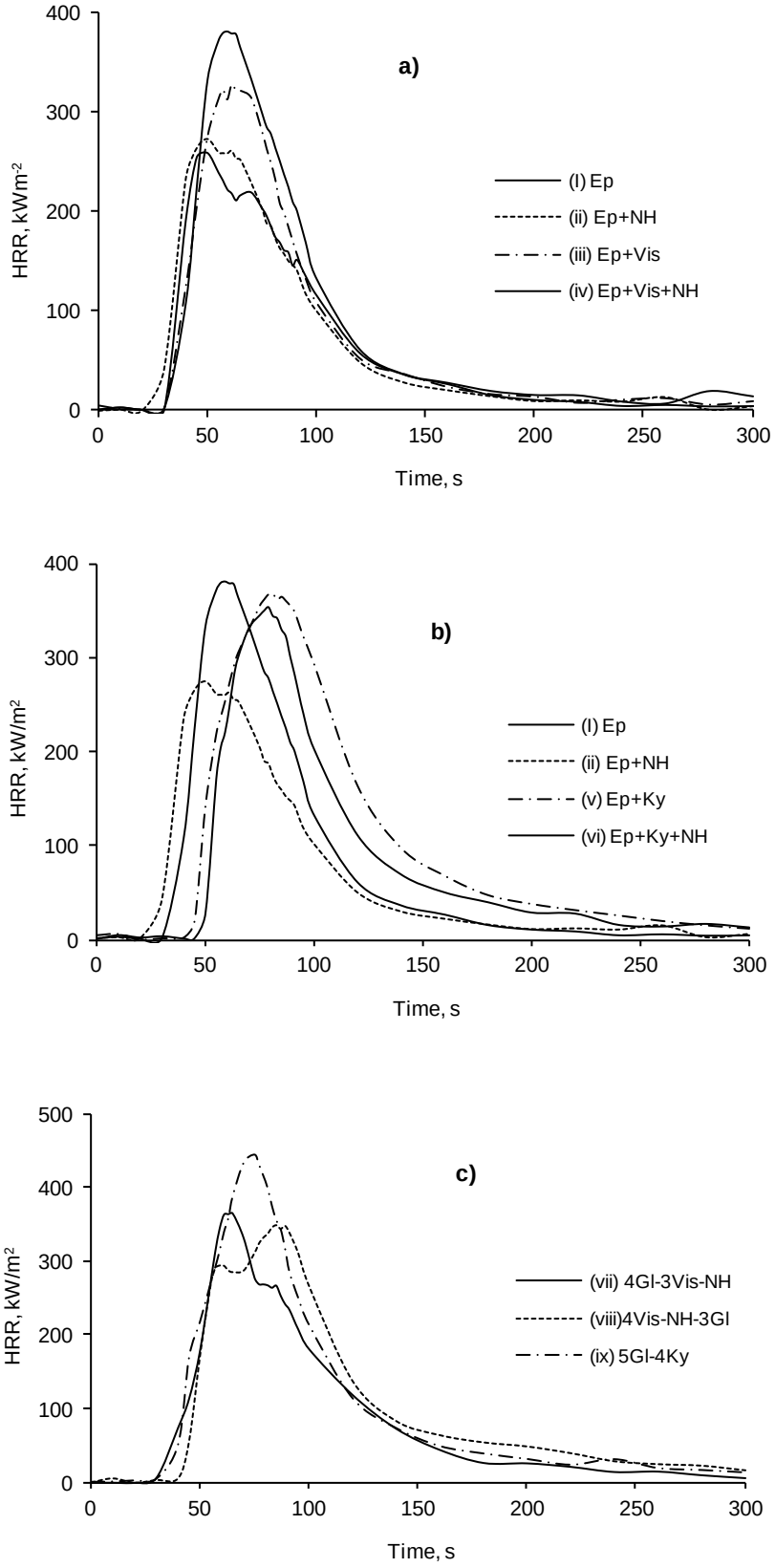
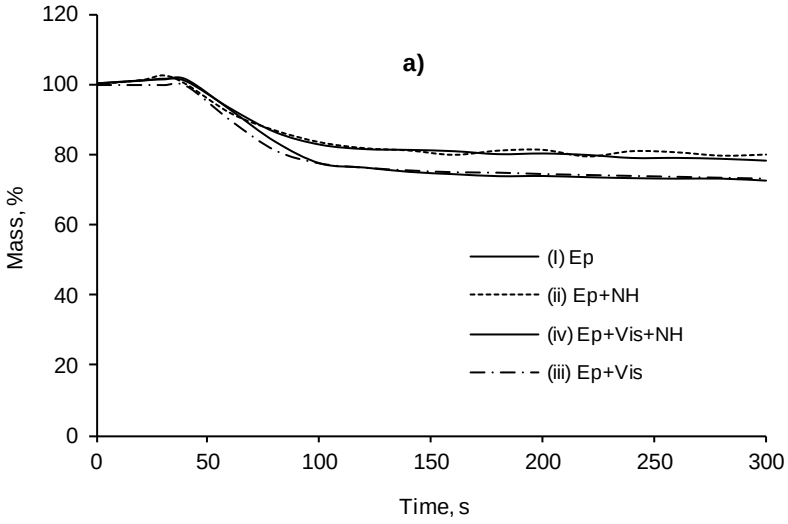


Figure 3. HRR versus time curves of samples (i)-(ix) at 50 kW/m^2 heat flux.



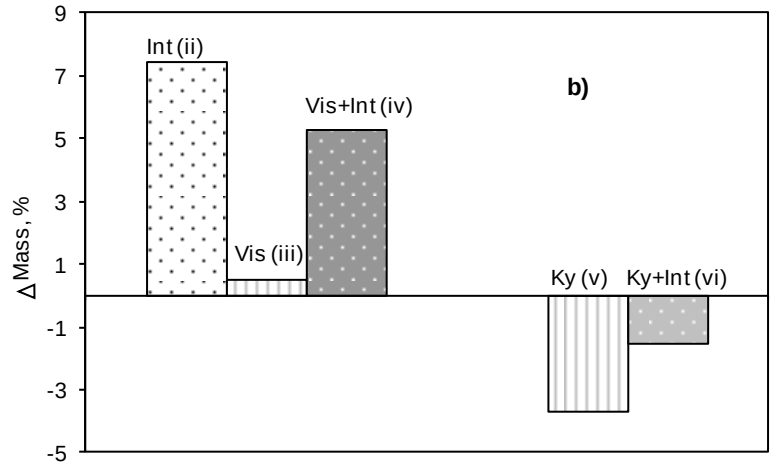


Figure 4. a) Mass loss curves of samples (i)-(iv) at 50 kW/m^2 heat flux and b) change in residual mass (Δ mass, %) of samples (ii)-(vi) compared to control sample (i).

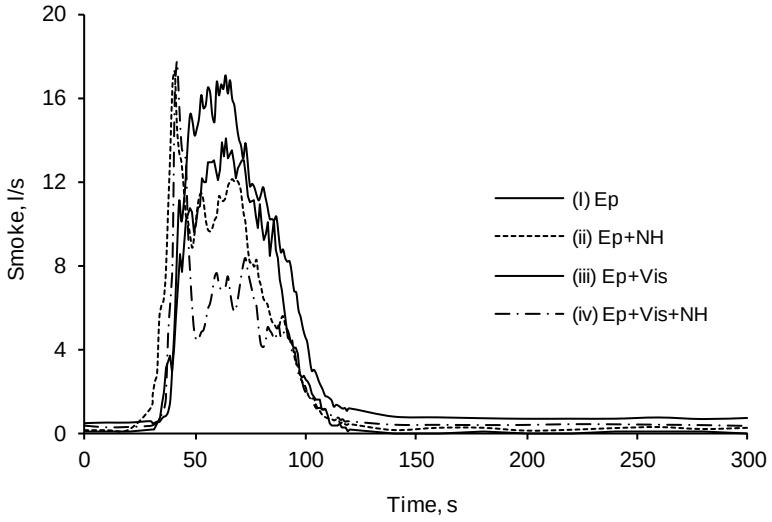


Figure 5. Smoke production curves of samples (i)-(iv) at 50 kW/m^2 heat flux.

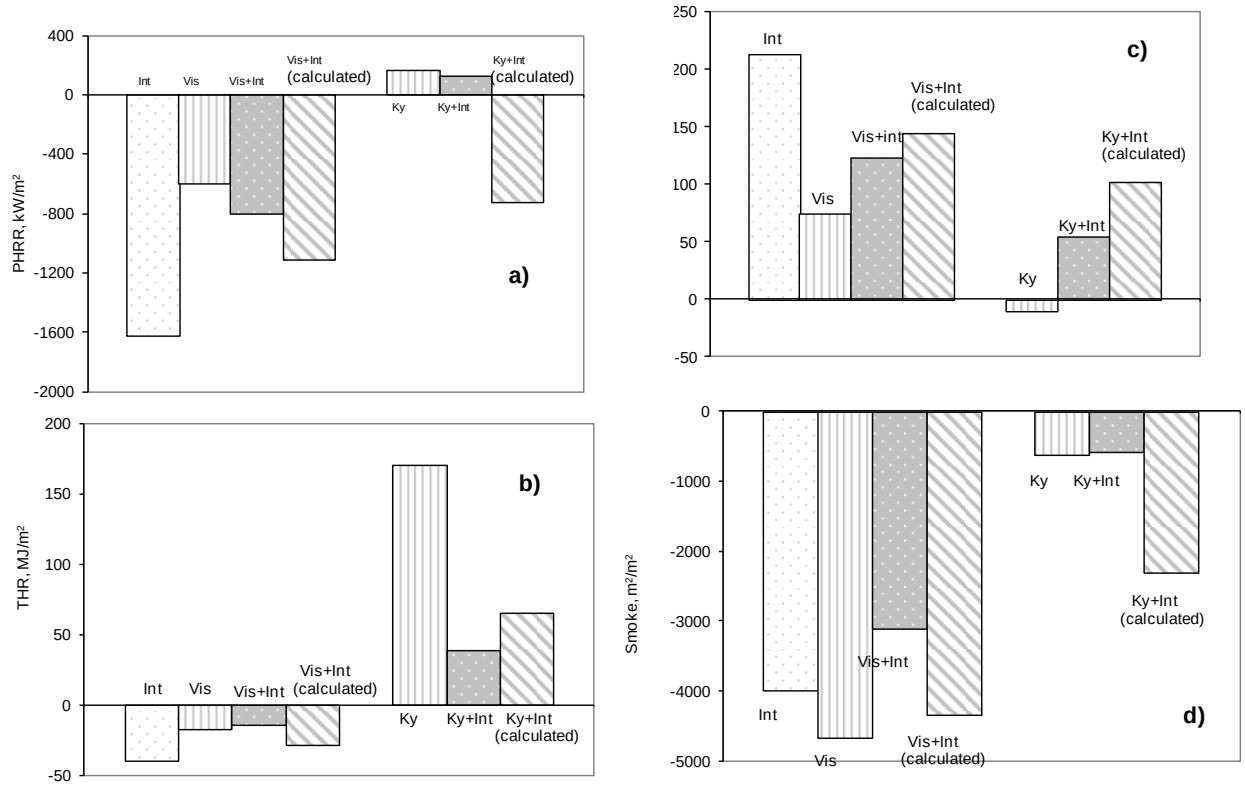


Figure 6. a) PHRR, b) THR, c) residual mass after 5 minutes exposure and d) smoke production per unit mass fraction of additives in samples (ii)-(ix).

Table 1. Physical and flammability (LOI) properties of composite laminate samples (i)-(ix).

Samples	Wt fraction (%) in composite				Thickness (mm)	LOI (%)
	Glass	Resin	FR fibre	Int		
(i) Ep	55.0	45.0	-	-	1.9	27.5
(ii) Ep+NH	53.0	42.3	-	4.7	2.0	35.2
(iii) Ep+Vis	53.0	42.3	4.7	-	2.1	28.1
(iv) Ep+Vis+NH	50.0	40.0	5.0	5.0	2.3	36.2
(v) Ep+Ky	53.0	42.3	4.7	-	2.4	27.7
(vi) Ep+Ky+NH	50.0	40.0	5.0	5.0	2.7	30.2
(vii) 4Gl-3Vis-NH	33.3	46.7	20.0 *		2.1	38.4
(viii) 4Vis-NH-3Gl	25.4	47.5	27.1 *		2.4	34.2
(ix) 5Gl-4Ky	38.8	52.9	8.3	-	2.4	27.8

* Vis –Int fabric

Table 2. Cone calorimetric results for composite samples (i)-(ix) at 50 kW/m^2.

Sample	TTI (s)	Flameout (s)	Peak HRR (kW/m^2)	TTP (s)	THR MJ/m^2	Average values from ignition to 5 min				Smoke At 300s (m^2/ m^2)
						HRR (kW/m^2)	H_c (MJ/kg)	CO yield (kg/kg)	CO_2 yield (kg/kg)	
(i) Ep	42	220	385	60	21.8	84	19.8	0.089	1.44	908
(ii) Ep+NH	35	225	278	48	18.3	61	18.8	0.074	1.11	648
(iii) Ep+Vis	41	219	329	61	19.4	65	16.6	0.089	1.21	614
(iv) Ep +Vis+NH	38	220	262	47	17.9	59	17.3	0.065	0.96	495
(v) Ep+Ky	51	291	367	79	28.8	96	19.0	0.077	1.33	817
(vi) Ep+Ky+NH	55	273	354	79	23.2	77	16.8	0.085	1.09	748
(vii) 4Gl-3Vis-NH	46	218	366	66	24.2	80	17.1	0.058	0.96	898
(viii) 4Vis-NH-3Gl	47	300	348	85	28.3	94	17.3	0.054	0.92	870
(ix) 5Gl-4Ky	44	287	445	74	28.4	94	19.8	0.092	1.29	807

Table 3. Derived cone parameters for composite samples (i)-(ix).

Sample	FIGRA kW/s	PHRR (kW/m^2)	THR (MJ/m^2)	H_c (MJ/kg)	Residual mass (%)	Smoke (m^2/ m^2)
(i) Ep	6.4					
(ii) Ep+NH	5.8					
(iii) Ep+Vis	5.4					
(iv) Ep +Vis+NH	5.6	231 (31)	16.5 (1.4)	16.0 (1.3)	30.1 (-2.1)	373 (122)
(v) Ep+Ky	4.6					
(vi) Ep+Ky+NH	4.5	269 (85)	25.9 (-2.7)	18.4 (-1.6)	25.9 (-4.7)	576 (172)
(vii) 4Gl-3Vis-NH	5.5	180 (186)	16.9 (7.3)	17.5 (-0.4)	47.3 (-19.1)	80 (818)
(viii) 4Vis-NH-3Gl	4.1	110 (238)	15.4 (12.9)	16.8 (0.5)	57.6 (-28.6)	-203 (1073)
(ix) 5Gl-4Ky	6.0	466 (-21)	39.2 (-10.8)	24.1 (-4.3)	20.0 (1.3)	1020 (-213)

Note : Values in the parentheses are the differences between calculated (presented here) and actual (from Table 2) values. Except for residual mass, negative differences indicate a “less-than-additive” effect.